

DESCRIPTION

PRODUCTION PROCESS FOR FINE CARBON FIBER

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Technical Field

The present invention relates to a production process for a fine carbon fiber such as a vapor grown carbon fiber and a carbon nanotube, specifically to a technique for continuously and stably producing a fine carbon fiber at a low cost.

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Background Art

~~Attentions are paid most to a carbon nanotube among fine carbon fibers. A carbon nanotube is a kind of vapor grown carbon fiber (VGCF) which has so far been researched, and a fine carbon fiber is variously called depending on a size of the fibers.~~In the field of fine carbon fibers, there has been significant research and focus on carbon nanotubes recently. A carbon nanotube is a vapor grown carbon fiber (VGCF) that is generally referred to by different names depending on the diameter of the fiber.. In general, a fiber having a fiber diameter of 1  $\mu\text{m}$  or more is called a vapor grown carbon fiber (VGCF); a fiber having a ~~fiber~~ diameter of 50 nm or less is called a carbon nanotube (CNT); and a fiber

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having a ~~fiber-diameter~~ of larger than 50 nm and smaller than 1  $\mu\text{m}$  ~~which falls in the middle of both of the above fibers~~ is called a carbon nanofiber (CNF).

5 A crystal structure of the above fine carbon materials assumes various forms ~~and includes~~, including a single-walled carbon nanotube (SWNT) ~~having a shape in which~~ wherein a single layer of a graphene sheet ~~constituted from~~ of carbon is wound into a cylindrical form, a multi-walled carbon nanotube (MWNT) having a  
10 structure in which several layers of graphene sheets are laminated like ~~a concentric circles~~ or an annual ring and a nanocone having a crystal structure falling in the middle of the both described above, that is, a conical structure in which crystal planes spread at a constant  
15 angle to a central axis thereof.

A fine carbon material ~~having of~~ a shape other than a tube includes a ribbon-like fine carbon material having a structure in which graphene sheets are laminated so that they cross orthogonally against a fiber direction,  
20 and a coil-like fine carbon material having an amorphous structure showing no crystallinity.

~~All these VGCF, CNF and CNT are fine carbon fibers, and therefore they have so far~~ usually been produced ~~usually by~~ crystallizing carbon from a gas phase by a  
25 thermal decomposition method ~~of using~~ hydrocarbons and CO

in the presence of transition metal catalyst.

~~The first step of~~Initial research in the present field ~~resides in research of a~~began with studies of vapor grown carbon fiber in the 1970s. In the development of  
5 initial VGCF, the fibers had a large diameter, and they were produced mainly by a fixed bed method (catalytic chemical vapor deposition method: CCVD method) in which reaction was carried out with a catalyst placed on a substrate or carried on a carrier. However, in an  
10 initial fixed bed method ~~having the purpose of~~ producing VGCF having a relatively large fiber diameter, the fiber was grown at a slow speed and produced in a low reaction yield, and therefore it was difficult to ~~industrially put~~ the method to practical use. However, ~~attentions were~~  
15 ~~paid to the point~~it was noted that a very fine fiber having a diameter of 50 nm or less could be produced, and it was industrialized by Hyperion Catalyst International Inc. in U.S. in 1990s.

On the other hand, a CVD (chemical vapor  
20 deposition) process in which reaction is carried out while allowing a catalyst to fluidize without using a carrier was developed in 1980s, and the yield was notably improved. In 1990s, ~~industrialization in~~ CNF having a diameter of a level of 100 nm ~~was succeeded~~were  
25 successfully industrialized (Showa Denko K. K. and

Nikkiso Co., Ltd.).

It was reported that a carbon nanotube having the finest fiber diameter could readily be produced by an arc process (Nature, 1991 (354), 56 to 58), and since then,  
5 ~~it has actively been tried~~there have been ongoing efforts to develop carbon fibers having a smaller fiber diameter. A production process for a single-walled carbon nanotube and a multi-walled carbon nanotube, each having a fine fiber diameter of 50 nm or less, particularly 10 nm or  
10 less, has come to be developed mainly by a process in which a fiber is produced by volatilizing carbon at a very high temperature as is the case with an arc process and a laser process and a CCVD process in which a carbon nanotube is formed on a fixed bed prepared by carrying a  
15 catalyst on a conventional ceramic carrier.

A carbon nanotube can be used as a filler material for an electron beam source and a composite material which are used for an image display apparatus and a semiconductor production apparatus, and in this case, it  
20 is preferred that the carbon nanotube is crystalline and straight and that it has a fine and even fiber diameter. If the carbon nanotube is not straight ~~and curled~~, the carbon fibers themselves are liable to be entangled to form flocks. If flocks are formed, they are less liable  
25 to be crushed, and it becomes difficult to align the

carbon fibers in use. Further, when the carbon fibers are added to a resin and the like as a filler material, they are less liable to be evenly dispersed, so that a composite having the desired characteristics is less  
5 ~~liable~~ likely to be obtained.

When an arc process, a laser process or a CVD process is applied in order to produce a carbon nanotube having the characteristics described above, the following problems ~~used to be involved therein~~ typically ensue.

10 In the arc process and the laser process, firstly, the productivity is low since it is difficult to make a large-scale production facility ~~thereof~~ large-scale, and it is difficult as well to make a production line continuous. Secondly, in the current arc process, the  
15 production efficiency is low since non-fibrous carbon is liable to be produced simultaneously, and it is difficult to separate and collect carbon nanotubes from non-fibrous carbon. Accordingly, it is difficult to produce a carbon nanotube having high quality suited to industrial  
20 products by the arc process and the laser process.

On the other hand, the CVD process is the most preferred process for mass production, but it is difficult to make the fiber diameter small in production by the CVD process, and the fiber diameter is liable to  
25 be uneven. Further, even if it is possible to make the

fiber diameter small by controlling the production conditions, there used to be the problem that a curled carbon nanotube is liable to be produced.

Accordingly, ~~attentions are paid to~~ Of more interest  
5 is a CCVD process in which a carbon nanotube having a fine fiber diameter is produced by using a fixed bed carried thereon with a catalyst. The production process of a carbon nanotube according to this CCVD process is almost the same as that of a CCVD process which had been  
10 investigated in the initial stage of developing VGCF described above, but it is different in that a porous carrier having fine pores such as zeolite is used as the carrier. Use of such specific carrier has made it possible to prepare fine catalyst particles making use of  
15 those pores and produce a very fine carbon nanotube (Kingsuk Mukhopadhyay, Akira Koshino, Toshiki Sugai, Nobuo Tanaka, Hisanori Shinohara, Zoltan Konya, B. Nagy; Chemical Physics Letters 303 (1997) 117).

Fig. 5 is a schematic ~~constitutional~~ drawing of a  
20 production process for producing a fine carbon fiber by a conventional batch type CCVD process. A production facility 200 shown in this drawing is equipped with a cylindrical reaction furnace 201 placed horizontally, a heater 202 disposed surrounding the periphery of the  
25 reaction furnace 201 in order to heat the reaction

furnace 201 from the outside, a raw material gas-feeding part 203 and a carrier gas-feeding part 204 which are connected to a right end side of the reaction furnace 201 as shown in the drawing and a supported catalyst-feeding part 205 connected to a left end side of the reaction furnace 201 as shown in the drawing. Further, a first carbon fiber-collecting part 206 for collecting the supported catalyst which is introduced into the reaction furnace from the supported catalyst-feeding part 205 and used for the reaction together with a fine carbon fiber produced thereon is connected to the right end side of the reaction furnace 201, and a bag filter 208 for receiving a reacted gas from the reaction furnace 201 and separating the reacted gas into the fine carbon fiber and a waste gas is connected to the left end side of the reaction furnace 201.

The bag filter 208 is provided with a gas-discharging part 208a and a solid discharging part 208b. A waste gas-treating apparatus 210 and a second carbon fiber collecting part 209 are connected to the gas-discharging part 208a and the solid discharging part 208b described above respectively, and the waste gas separated by the bag filter 208 is discharged into the waste gas-treating apparatus 210, while the fine carbon fiber which is solid is collected in a second carbon fiber-recovering

part 209.

In the production facility for a fine carbon fiber shown in Fig. 5, the supported catalyst such as a catalyst carried on zeolite is introduced from the supported catalyst-feeding part 205 into the reaction furnace 201 charged with a raw material gas and a carried gas, and the fine carbon fiber is allowed to grow on the supported catalyst by thermal decomposition reaction. The supported catalyst holding the fine carbon fiber on the surface thereof is collected in the first carbon fiber-collecting part 206. Also, the reacted gas, after being used for the reaction, is discharged into the bag filter 208 from the reaction furnace 201, and it is separated into the fine carbon fiber and the waste gas by the bag filter 208. Then, the fine carbon fiber separated by the bag filter 208 is collected into the second carbon fiber-collecting part 209, and the waste gas is sent to the waste gas-treating apparatus 210. Thus, the fine carbon fiber can be produced by the CCVD process using the production facility shown in Fig. 5.

On the other hand, a large amount of a carrier gas (hydrogen, inert gas and the like) has to be introduced into a reaction furnace in producing a vapor grown carbon fiber and a carbon nanotube by the CCVD process and the CVD process described above, and therefore it is a large



factor by ~~which~~ in increasing the production cost ~~grows~~  
high.

Further, in the production by the CCVD process and  
the CVD process described above, the remaining unreacted  
5 raw material gas, as well as ~~low boiling components and~~  
~~high boiling components which are by-products~~ are  
contained in the reacted gas after used for the reaction,  
and ~~therefore they~~ can not be discharged to the outside  
as they are in order to prevent the environment from  
10 being polluted. Accordingly, waste gas treatment such as,  
for example, incineration treatment and adsorption  
treatment is required for discharging the above gas to  
the outside. Since a large amount of a carrier gas is  
used, as described above, in the production by the CCVD  
15 process and the CVD process, an amount of the waste gas  
itself is increased, and a cost for waste gas treatment  
grows large.

Further, sulfides such as hydrogen sulfide and  
thiophene are added in ~~a certain case~~ some cases for the  
20 purpose of accelerating the carbon fiber producing  
~~reaction of producing a carbon fiber~~. In this case, a  
sulfur compound is contained in the waste gas, and  
therefore it has to be removed. However, an amount of the  
waste gas itself is large as described above, so that he  
25 treating cost is increased very much.

As described above, the production cost can not help growing high in the CCVD process and the CVD process because of the large amounts of the gas used and the waste gas amount, ~~and it used to be a large~~ This is a  
5 generally acknowledged problem in mass-producing a fine carbon fibers.

An object of the present invention is to provide a production process in which a fine carbon fiber such as a vapor grown carbon fiber and a carbon nanotube, each  
10 having an optional fiber diameter, particularly a fine fiber diameter, can continuously and stably be produced at a low cost.

#### Disclosure of the Invention

15 ~~Earnest~~ Investigations ~~repeated~~ by the present inventors ~~in order~~ to solve the problems described above have resulted in finding that: in a process for producing a fine carbon fiber by a ~~thermal decomposition process~~ (CVD process and CCVD process) of CO and an organic  
20 compound using ultra fine particles ~~comprising~~ of a transition metal as a catalyst, use of at least one organic compound containing a ~~VI~~ Ban IUPAC group 16 element ~~(in~~ from the periodic table of elements) ~~in a molecule~~ as a raw material makes it possible to produce a  
25 fine carbon fiber having high quality and a very fine

fiber diameter; and that use of the above organic compound for the raw material makes it possible to readily separate and recover reaction by-products and the unreacted raw material from the reacted gas; and recycling of the reacted gas into a reaction furnace makes it possible to reduce the amounts of a carrier gas and a waste gas.

The production process for a fine carbon fiber according to the present invention comprises introducing a raw material gas comprising an organic compound, a carrier gas comprising hydrogen and/or an inert gas, and a catalyst comprising ultra fine particles containing at least one transition metal into a reaction furnace to produce a fine carbon fiber ~~in the reaction furnace described above~~ by thermal decomposition reaction, wherein an organic compound containing a VIBan IUPAC group 16 element ~~in the periodic table of elements in a molecule~~ is used as the raw material organic compound, and the reaction is carried out at a pressure of  $2 \times 10^5$  Pa or less. After collecting the fine carbon fiber from a reacted gas used for producing the fine carbon fiber, the reacted gas is further cooled, and the fine carbon fiber is collected by a different separating and collecting apparatus having higher separating ability. Then, at least a part of the above reacted gas,

preferably gas obtained by removing by-products and unreacted gas from the reacted gas is reintroduced into the reaction furnace by a recycling means connected to the reaction furnace described above and used.

5        ~~Not only the fine carbon fiber is produced in the reaction furnace, but also low boiling components, high boiling components and H~~hydrogen gas ~~are produced as and~~ other by-products are produced by the decomposition reaction, and they are contained in the gas coming out  
10       from the reaction furnace together with the unreacted raw material gas and the carrier gas. If the above by-products are stuck onto the inner wall of the production facility, the pipelines and equipments ~~constituting of~~ the production facility are likely to be clogged.

15       In the present invention, an organic compound containing a ~~VIB~~IUPAC group 16 element ~~in the periodic table in a molecule~~ is used as the raw material. The ~~VIB~~IUPAC group 16 element is preferably oxygen ~~and or~~ sulfur, particularly oxygen. For example, when a compound  
20       containing oxygen is used, water, CO, CO<sub>2</sub> and hydrogen are produced as by-products.

      In reference to the organic compound containing a ~~VIB~~IUPAC group 16 element ~~in a molecule~~, the compound containing oxygen includes alcohols, ketones, phenols,  
25       ethers, aldehydes, organic acids and esters.

To be specific, it includes, for example, methanol, ethanol, propanol, cyclohexanol, acetone, methyl ethyl ketone, acetophenone, cyclohexanone, phenol, cresol, formaldehyde, acetaldehyde, formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, adipic acid, dimethyl ether, diethyl ether, dioxane, methyl acetate and ethyl acetate.

The sulfur compound includes thiols, thioethers and thiophenes, and thioethers can particularly be used.

The above raw material organic compounds can be fed into the reaction furnace by spraying in the form of gas, liquid, solution or solid.

The above compounds can be used alone or in a mixture of two or more kinds thereof.

The fine carbon fiber of the present invention is produced by the CVD process or the CCVD process, and ultra fine particles comprising a transition metal are used as the catalyst.

The transition metal includes, for example, iron, cobalt, nickel, yttrium, titanium, vanadium, manganese, chromium, copper, niobium, molybdenum, palladium, tungsten and platinum. In addition to the metals of simple substances, the compounds thereof can be used as the catalyst. Further, they may be used alone or in combination of two or more kinds selected from them. The

larger catalytic effect is obtained depending on the combination.

In respect to the form of the compounds, ~~the~~ organic compounds, ~~the~~ inorganic compounds or ~~the~~ a combination thereof can be used. For example, ferrocene, nickelocene and cobaltocene can be used as the organic compounds. Also, the inorganic compounds may assume any form of oxide, nitrate, sulfate and chloride.

Further, in order to raise an efficiency of fiberization, a sulfur compound such as sulfur,  $H_2S$ ,  $CS_2$ ,  $SO_2$  and thiophene may be added when putting the raw material and the catalyst into the reaction furnace. When using such compound, the same effect can be obtained even if the raw material organic compound is an organic compound containing no ~~VIB~~ IUPAC group 16 element ~~in a~~ molecule such as (for instance, hydrocarbons).

The catalysts may be fine particles ~~themselves~~ of the metals or the compound described above (CVD process), and the metals or the compounds described above may be carried on fine particles of an inorganic carrier (CCVD process). For example, alumina, zeolite, carbon, magnesia and calcia can be used as the inorganic carrier.

An introducing method of the catalyst may be any of a method of gasifying alone, a method of gasifying after mixed with the raw material carbon source, or a method of

diluting with a carrier gas and a method of dissolving in the raw material carbon source and feeding in a liquid form.

5 In the present invention, carbon having no crystallinity and the ~~VIB~~ IUPAC group 16 element participate in the reaction by using ~~the catalyst~~ comprising a transition metal catalyst and using the an organic compound containing a ~~VIB~~ IUPAC group 16 element in a molecule as the raw material, whereby  
10 ~~capable of being obtained are single-walled and multi-walled carbon nanotubes in which~~ of a high purity is high and having a fiber diameter is as fine as of 10 nm or less and ~~which has an axial chiral structure~~ can be obtained.

15 According to the production process for ~~the fine~~ carbon fiber of the present invention, the reacted gas used for producing the fine carbon fiber is re-introduced ~~again into the reaction furnace by a recycling means,~~ whereby the reacted gas which has ~~so far~~ previously been entirely discharged to the outside can effectively be  
20 used. This makes it possible to reduce ~~a use amount~~ the amounts of ~~the carrier gas as well as an amount of~~ the used and waste gas produced, and ~~therefore both of a~~ cost for the carrier gas and a cost for treating the waste gas can be reduced thereby reducing both production  
25 and waste treatment costs. Accordingly, it becomes

possible to reduce a ~~cost relating to the~~ production cost  
of ~~the~~ fine carbon fiber via the inventive process as  
compared with ~~these of more conventional ones~~ processes.  
In particular, ~~a~~ the concentration of ~~the~~ raw material  
5 gas in the reaction furnace has to be maintained at or  
below a specific dilute dilution level in order to  
produce a carbon nanotube having a fine fiber diameter of  
10 nm or less. ~~That is, an~~ This can be effectuated by  
increasing the amount of the carrier gas ~~is increased,~~  
10 ~~and thereby~~ diluting the concentration of the raw  
material ~~is diluted.~~ In such sense, ~~it~~ It is cost-  
effective to recycle the reacted gas for this purpose.

The production process for the fine carbon fiber of  
the present invention is a process for producing a fine  
15 carbon fiber by a thermal decomposition method using the  
~~VIB-IUPAC group 16~~ element-containing organic compound as  
the raw material and using ultra fine particles  
~~comprising of~~ a transition metal as the catalyst, ~~and~~  
~~the~~ The production process comprises a reaction furnace  
20 for allowing a thermal decomposition reaction ~~in an~~  
~~inside thereof~~ therein to ~~proceed to~~ produce a fine carbon  
fiber, a raw material gas-feeding part for feeding a raw  
material gas into the reaction furnace, a carrier gas-  
feeding part for feeding a carrier gas into the reaction  
25 furnace, a carbon fiber-separating apparatus for



separating and collecting the fine carbon fiber produced in the reaction furnace from a reacted gas, a recycling means for cooling the reacted gas to introduce it again into the reaction furnace and, preferably, an apparatus for condensing and separating ~~condensing~~ condensable components contained in the above reacted gas.

In the production of the fine carbon fiber of the present invention, the separating apparatus described above is connected to the carbon fiber-collecting apparatus; ~~the~~ The fine carbon fiber separated from the reacted gas by the separating apparatus is collected in the carbon fiber-collecting apparatus; ~~the~~ The reacted gas coming out from the separating apparatus is cooled, and then the cooled gas is allowed to pass through another separating apparatus to further collect the fine carbon fiber. The gas coming out from the carbon fiber-collecting apparatus can be directly discharged after waste gas treatment. In the process of the present invention, however, the gas remaining after collecting the fine carbon fiber is recycled to the reaction furnace by the recycling means described above. In this case, the above gas is further cooled to condense ~~condensing~~ components such as water produced by the reaction and the unreacted raw material, and then the gas is introduced into the reaction furnace after separating ~~them~~ the

~~condensates from it. On the other hand, the~~  
~~condensate separated is~~ condensates are subjected to  
waste liquid treatment and then discharged. Further, the  
unreacted raw material can be separated from the  
5 condensate and recycled as the raw material.

~~Further, the~~ In some cases, unreacted raw material,  
produced water and high boiling by-products ~~are stuck in~~  
~~a certain case and~~ adhere to the fine carbon fiber ~~which is~~  
~~the product~~ obtained from the separating and collecting  
10 apparatus, and therefore the product is once heated to  
vaporize ~~them~~ these unwanted substances, whereby the  
~~product having a higher purity~~ product can be obtained.  
The raw material compound can be separated from the  
vaporized components and recycled as the raw material.

15 The raw material compound can be separated from the  
condensate and ~~the vaporized components each~~ described  
above by ~~one~~ a method of distillation, adsorption ~~and or~~  
membrane separation or a method in which two or more of  
them are combined.

20 ~~If assuming such constitution, a collecting rate of~~  
~~the fine carbon fiber to a charged amount of the raw~~  
~~material can be enhanced by collecting the fine~~ In such a  
process, more carbon fiber ~~as well from~~ can also be  
collected from the reacted gas that is cooled after  
25 separating the initially produced fine carbon fiber from

the reacted gas, and an increase in the production cost brought about by reduction in the collecting rate can be prevented further mitigating production costs by increasing overall process yield.

5           The fine carbon fiber produced by thermal decomposition reaction has a very small bulk density and is light, so that the total amount thereof or the carbon fiber peeled from the catalyst floats in the reaction furnace. Accordingly, the reacted gas discharged from  
10 the reaction furnace is accompanied with the fine carbon fibers and the reaction by-products. If gas used for recycling is reintroduced into the reaction furnace as it is mixed with the fine carbon fiber and subjected to the reaction, carbon grows further on the fine carbon fibers  
15 to enlarge a fiber diameter (broaden a width of a fiber diameter), so that the desired fiber diameter is not likely to be obtained. Accordingly, the fine carbon fiber contained in the reacted gas is removed in the present invention by providing the separating means  
20 described above so that only the gas component is reintroduced into the reaction furnace, whereby the fiber diameter is prevented from becoming large. This makes it possible to stably produce the fine carbon fiber having a desired fiber diameter.

25           Also, if solids such as the fine carbon fiber and

high-boiling-point by-products contained in the reacted gas are circulated in the insides of the reaction furnace and the recycling means, they are likely to be stuck on the insides of pipes connecting them, ~~to clog the pipes causing clogs.~~ According to the ~~constitution described above~~present invention, however, the solids (such as the fine carbon fiber) and the condensates are separated by the separating apparatus, and the gas reintroduced into the reaction furnace does not contain the solids and the condensate. Accordingly, ~~such trouble as described above~~clogs and related problems can be prevented ~~beforehand~~, and it becomes possible to stably produce the fine carbon fiber.

In the production process for the fine carbon fiber of the present invention, a filter, a cyclone and a device obtained by combining them, each of which has a function to efficiently separate solids from gas, are suitably used as a separating means. The most suited one can be selected from the above filter and cyclone according to an amount and a temperature of the gas.

For example, when an amount of the reacted gas is large, an amount of the fine carbon fiber collected in the separating means becomes large as well, and therefore a load charged on one filter has to be controlled so that it does not become so large. In this case, a combination

of a filter having a large mesh and a bag filter having a fine mesh or combination of a filter and a cyclone are recommendable.

5 The gas coming out from the reaction furnace stays, though depending on a temperature of the reaction furnace, in a high temperature of about 600°C or higher. When using a bag filter, ~~the gas ef-at~~ at such a high temperature ~~can-not~~ cannot be allowed to pass through it, and therefore separation by the bag filter described above is  
10 preferably carried out after the temperature of the reacted gas is lowered. To be specific, a cooling means such as a water-cooled jacket is provided in a path from the reaction furnace or the carbon fiber-collecting part to the separating apparatus to cool the reacted gas. The  
15 gas is cooled down to a temperature range between 40°C or higher-te and 150°C or lower (preferably 100°C or lower) by the above cooling means, and then separation by the bag filter is carried out. A solid product which is less  
20 liable to be cooled is mixed in the reacted gas in a certain case, and therefore it is advisable to use a bag filter which can endure as high a temperature as possible for the filter.

In the production process for the fine carbon fiber of the present invention, the gas obtained after  
25 separating the fine carbon fiber is further cooled to

recover the unreacted raw material organic compound and the condensate such as produced water, and they can be separated by an apparatus in which two or more methods of distillation, adsorption and membrane separation are combined.

Next, in the production process for the fine carbon fiber of the present invention, when recycling the reacted gas, a temperature of the gas reintroduced into the reaction furnace is preferably controlled to 40°C or higher.

Substances produced in the reaction furnace are not restricted only to the fine carbon fiber, and the unreacted hydrocarbon and the organic compounds of low boiling point components and high boiling point components are contained as by-products in the reacted gas discharged from the reaction furnace. If the organic compounds are stuck on the inner wall of the production facility, they are likely to clog pipelines constituting the production facility. A measure for preventing these pipelines from being clogged is required in order to safely carry out the production. Various investigations on production conditions ~~therefor repeated by the present inventors~~ have resulted in finding that if a temperature of the gas which passes through at least the recycling means described above and is reintroduced into the

reaction furnace is controlled to 40°C or higher, the organic compounds are almost completely prevented from being deposited and that as a result, the pipelines can be prevented from being clogged. That is, organic compounds can be controlled so that they are not deposited from the raw material gas, the reacted gas and the recycled gas in the facility by controlling a temperature of the gas when passing through the recycling means in which the temperature of the gas becomes the lowest in the whole of the production facility to 40°C or higher. Accordingly, when the temperature of the gas is lower than 40°C in a position where the temperature of the gas becomes the lowest, the gas is, if necessary, thermally insulated by a means such as covering or heated so that it is maintained at 40°C or higher.

Also, the temperature of the gas which passes through the inside of the recycling means described above and is reintroduced into the reaction furnace is more preferably 60°C or higher. That is, if the temperature of the gas is 60°C or higher, the organic compounds can more effectively be inhibited from being deposited from the gas, and therefore further stable production shall be possible.

In respect to a position where the reaction gas described above is reintroduced into the reaction furnace,

it may be returned directly to the reaction furnace or may be mixed with the raw material gas and/or the carrier gas and then reintroduced into the reaction furnace. In the case of the latter, for example, in the case where a liquid raw material is gasified for use, the reacted gas is preferably heated to a prescribed temperature in advance so that the raw material gas and the reacted gas mixed are not liquefied.

Next, in the production process for the fine carbon fiber of the present invention, 20 % or more of the reacted gas described above is preferably reintroduced into the reaction furnace by the recycling means and used. ~~Assuming the above constitution~~ This level of gas recycling and reintroduction makes it possible to obtain a marked cost-reducing effect by reduction in an amount of the carrier gas and an amount of the waste gas. It is more preferably controlled to 50 % or more, but if an organic compound is used for the raw material gas, hydrogen is produced by thermal decomposition reaction, so that an amount of hydrogen contained in the gas coming out from the reaction furnace grows larger than an amount of hydrogen introduced as the carrier gas. Accordingly, the increment of hydrogen due to gas generation has to be discharged. That is, an amount of the gas reintroduced into the reaction furnace for recycling is up to the same



amount, at the most, as that of the carrier gas to be introduced into the reaction furnace.

In the production process for the fine carbon fiber of the present invention, the inside of the recycling means described above is preferably a positive pressure to an atmospheric pressure.

In the production process for the fine carbon fiber of the present invention, when reusing the reacted gas by circulating, the reacted gas likely contains ~~surely~~ hydrogen gas and the raw material organic compound. If oxygen is mixed in the hydrogen gas and the organic compound, a fire and large explosion are likely to be brought about. In order to prevent ~~them~~ such an event, the inside of the system in the facility, including the pipelines, ~~has~~ have to be maintained at a positive pressure ~~without being a negative pressure~~. In particular, a suction side of the gas circulating means for circulating the gas in the facility is most liable to ~~be cause~~ a negative pressure, and therefore a measure is preferably undertaken so that this part does not become a negative pressure.

To be specific, the following can be given as the measure for preventing a negative pressure:

(1) increasing a diameter of a pipeline at a suction side of the gas circulating means described above as much as

possible,

(2) operating while monitoring a pressure of a suction side of the gas circulating means described above,

(3) controlling so that the facility can be stopped when  
5 the pressure becomes a negative pressure,

(4) controlling so that a safety gas (for example, inert gas such as  $N_2$ , Ar and the like) can be introduced into the facility when the pressure becomes a negative pressure and

10 (5) constituting the system having a circulating system for controlling pressure before and after the gas circulating means.

In the production of the fine carbon fiber of the present invention, a raw material gas fed from a raw  
15 material gas-feeding source and a carrier gas fed from a carrier gas-feeding source may be fed separately to the reaction furnace, or may be fed in a mixture of a reaction gas. In the case of the latter, the raw material and the carrier gas are mixed to produce the  
20 reaction gas, and the reaction gas is introduced into the reaction furnace.

Also, when the reacted gas is recycled, the recycled gas is preferably mixed with the carrier gas and introduced into the reaction furnace.

25 For example, when an organic compound which is

liable to be liquefied is used for the raw material gas,  
the raw material gas can be prevented from being  
liquefied by assuming the above constitution, and  
therefore clogging of the pipelines and an instability in  
the raw material concentration can be prevented.  
Accordingly, the facility can stably be operated, and  
this makes it possible to enhance homogeneity of the fine  
carbon fiber produced.

Further, an amount of the carrier gas which is  
newly charged can be reduced, and an amount of the waste  
gas can be reduced as well, so that both of a carrier gas  
cost and a waste gas treatment cost can be reduced.  
Accordingly, the fine carbon fiber can readily be  
produced at a low cost by means of the CVD process and  
the CCVD process by using the production facility for the  
fine carbon fiber of the present invention.

#### Brief Description of the Drawings

Fig. 1 is a constitutional drawing schematically  
showing the production process for the embodiment of the  
reference example.

Fig. 2 is a constitutional drawing schematically  
showing the production process for the first embodiment.

Fig. 3 is a constitutional drawing schematically  
showing the production process for the second embodiment.

Fig. 4 is a constitutional drawing schematically showing the production process for the third embodiment.

Fig. 5 is a constitutional drawing schematically showing the production process by a conventional batch type CCVD process.

#### Best Mode for Carrying out the Invention

The embodiments of the present invention shall be explained below with reference to the drawings.

#### Embodiment of the reference example

Fig. 1 is a constitutional drawing schematically showing the production process for the fine carbon fiber showing the embodiment of the reference example which is the base of the present invention. The production process of the present invention shown in the above drawing is a production process for producing a fine carbon fiber by the CCVD process, and it is constituted from a cylindrical reaction furnace 3, a raw material gas-feeding part 2, a carrier gas-feeding part 1 and a catalyst-charging apparatus 20 which are connected to an inlet side end of the reaction furnace, a fine carbon fiber-separating and collecting apparatus 4 connected to an outlet side end of the reaction furnace 3, a fine carbon fiber-collecting tank 8 connected to a lower part

of the fine carbon fiber-separating and collecting apparatus 4, a reacted gas-cooling apparatus 6 connected to an upper part of the same, a second fine carbon fiber-separating and collecting apparatus 5 for further separating the fine carbon fiber from a cooled gas and a waste gas-treating apparatus 12.

When producing the fine carbon fiber by the production process shown in Fig. 1, the reaction furnace 3 is first heated and maintained at 600°C or higher to 1250°C or lower by a heater equipped to the reaction furnace 3. The foregoing temperature of the reaction furnace shows one example of the production conditions, and actually, it is set to the optimum condition depending on combination of the kind of a carbon source (an oxygen-containing organic compound and the like) which is used as a raw material, the kind of a catalyst and the kind of a carrier gas.

Next, a raw material gas comprising an organic compound containing a ~~VIBan~~ IUPAC group 16 element in a molecule is introduced as a carbon source for a fine carbon fiber into the reaction furnace 3 from the raw material-feeding part 2, and a carrier gas comprising hydrogen, methane or an inert gas is introduced into the reaction furnace 3 from the carrier gas-feeding part 1. Further, a catalyst for causing the reaction of

fiberizing carbon in the reaction furnace 3 is introduced into the reaction furnace 3 together with the above gases. Then, the raw material gas is decomposed with heat in the reaction furnace 3, and a fine carbon fiber is produced by the action of the catalyst.

Next, the fine carbon fiber produced is sent to the fine carbon fiber-separating and collecting apparatus 4 together with the gas in the reaction furnace. Then, the fine carbon fiber is separated from a reacted gas by the fine carbon fiber-separating and collecting apparatus 4 and sent to the fine carbon fiber tank 8. The gas coming out from the fine carbon fiber-separating and collecting apparatus 4 is cooled to 40°C or higher to 150°C or lower and comes into the second fine carbon fiber-separating and collecting apparatus 5, wherein the fine carbon fiber is further collected by a separating device which can be used for a low temperature gas, such as a bag filter, to be stored in the collecting tank 8. On the other hand, the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is discharged to the outside of the system after treated by the waste gas-treating apparatus.

First embodiment:

~~Next, the~~The first embodiment of the present

invention shall be explained with reference to Fig. 2.

The same elements as the constitutional elements shown in Fig. 1, among the constitutional elements shown in Fig. 2, shall be represented with the same symbols, and detailed explanations therefor shall be omitted (the same shall apply to the following embodiments).

Fig. 2 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the first embodiment of the present invention.

The production process of the present invention shown in the above drawing is a production process for producing a fine carbon fiber by the CCVD process, and it is a process equipped with a recycling apparatus. That is, in the embodiment of the reference example described above, the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is discharged to the outside of the system after treated by the waste gas-treating apparatus. However, this is a process in which a part thereof is circulated to the reaction furnace by a gas-circulating blower 9. In this process, a circulated gas and a discharged gas can freely be controlled, and therefore a gas-circulating amount in the reaction system can readily be controlled.

This makes it possible to reduce an amount of a carrier gas made up, and as a result to reduce an amount

of a waste gas. Further, the unreacted raw material gas, the VI-IUPAC group 16 element-containing compound and the by-products can be returned to the reaction system, and therefore the yield can be increased.

5 Further, the fine carbon fiber is separated at two stages by the separating apparatus 4 and 5, and therefore the fine carbon fiber is not mixed in the circulated gas, so that the fiber can be prevented from becoming thick by allowing carbon to further grow on the fiber.

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Second embodiment:

Fig. 3 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the second embodiment of the present invention.

15 The production process of the present invention shown in the above drawing is a production process in which in the first embodiment described above, a part of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is further cooled by another

20 cooling apparatus 7 which is different from the cooling apparatus 6 before the gas is circulated to the reaction furnace by the gas-circulating blower 9, so that reaction by-products such as water and the non-decomposed raw material organic compound which are contained in the gas

25 are condensed and then separated and removed from the gas



to circulate the gas. The condensate separated is sent to a moisture separator 11 via a condensate tank 10 to recover the condensate such as water and an organic compound gas, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the moisture separator 11 is discharged to the outside of the system after treated by a waste water-treating apparatus 15.

In the above process, water and organic compounds having a relatively high boiling point are not contained in the circulated gas, and therefore the moisture concentration is controlled to a lower level. Accordingly, the moisture can be inhibited from being condensed, and the pipelines can be prevented from being clogged.

Third embodiment:

Fig. 4 is a constitutional drawing schematically showing the production process for the fine carbon fiber which is the third embodiment of the present invention. The second embodiment described above is a process in which only the gas circulated to the reaction furnace by the gas-circulating blower 9 out of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus

7 to further lower a temperature of the gas, so that the reaction by-products contained in the gas such as water and the non-decomposed raw material organic compound are condensed and then separated and removed from the gas to circulate the gas. However, the production process of the present invention shown in the above drawing is a production process in which the total amount of the gas coming out from the second fine carbon fiber-separating and collecting apparatus 5 is cooled by the cooling apparatus 7 to separate condensate contained in the above gas. A part of the gas remaining after separating the condensate is circulated to the reaction furnace by the blower 9, and the residual gas is sent to a waste gas-treating apparatus 12 and discharged to the outside of the system after treated. On the other hand, the condensate separated is sent to a moisture separator 11 via a condensate tank 10 to recover the condensate such as water and the organic compound, and this gas is circulated as well to the reaction furnace 3. The condensate stored in the gas-liquid separator 11 is discharged to the outside of the system after treated by a waste water-treating apparatus 15.

In this process, not only the total amount of the effective organic compound is recycled, but also water and organic compounds having a relatively high boiling

point are not contained in the circulated gas, and therefore a moisture concentration in the system is controlled to a lower level. Accordingly, the moisture is inhibited from being condensed, and the pipelines are prevented from being clogged. Further, components to be condensed are not entered into the waste gas-treating apparatus, and therefore a load charged thereon is reduced.

#### Examples

The present invention shall be explained below in further details with reference to examples and a reference example, but the present invention shall by no means be restricted to the examples described below.

#### Reference Example

Carried out by the process shown in Fig. 1. A reaction furnace used is of a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  is heated from the outside, and it is a reaction furnace of a rotary type in which the reaction tube can be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source and continuously charged at a flow rate of 7.4 NL/minute. Argon was used for a carrier gas, and a flow rate thereof was set to 5

NL/minute. A catalyst that was prepared by carrying two components of molybdenum and cobalt on magnesium oxide, having an average particle diameter of 0.1  $\mu\text{m}$  or less, according to a conventional method and then activating it in an inert gas was charged at a rate of 15 g/min. The reaction temperature was set to 810°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 3 rpm.

As a result of the reaction, ~~obtained was~~ 19 g/min of crude CNT was obtained, which includes the catalyst and volatile components, and ~~is was~~ collected in a CNT-collecting tank. Actual CNT content in the crude CNT was 3.8 g/min.

#### Example 1

The present example was carried out by the process shown in Fig. 2. Used for a reaction furnace was a reaction tube of a rotary type having a structure in which the same SiC-made reaction tube having an inner diameter of 200  $\phi$  as in the reference example was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at

a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated in an inert gas and then charged at a rate of 15 g/min.

5 The reaction temperature was set to 805°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 2 rpm. Recycled was the reacted gas (containing unreacted ethyl alcohol and decomposition products)  
10 corresponding to 20 % of argon gas contained in the reacted gas at the outlet, and the ~~remained~~remaining gas was sent to a waste gas-treating system. Accordingly, the carrier gas in the furnace was argon gas and was controlled so that a newly charged argon gas was 4 NL/min.

15 As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.3 g/min, and a—CNT content in the crude CNT was 4.0 g/min. The CNT yield was more improved by 0.2 g/min than the case where recycling was not carried out, and an  
20 amount of argon charged was reduced by 20 %.

#### Example 2

The present example was carried out by the process shown in Fig. 3. Used for a reaction furnace in the  
25 present example was a reaction tube of a rotary type

having a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 815°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The reacted gas corresponding to 50 % of argon gas contained in the reacted gas at the outlet was recycled to the reaction system after cooled by a cooler 7 to remove water by a moisture separator. Then, the ~~remained~~remaining gas was sent to a waste gas-treating system. The carrier gas in the furnace comprised 3 NL/min as a newly charged portion and 3 NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude CNT which were collected in a CNT-collecting tank were 19.6 g/min, and a-CNT content in the crude CNT was 4.2 g/min. The CNT yield was more improved by 0.4 g/min than

the case where recycling was not carried out, and an amount of argon charged was reduced by 50 %.

### Example 3

5           The present example was carried out by the process shown in Fig. 4. Used for a reaction furnace in the present example was a reaction tube of a rotary type having a structure in which an SiC-made reaction tube having an inner diameter of 200  $\phi$  was heated from the outside and in which the reaction tube could be rotated at a constant speed. Ethyl alcohol was used for a raw material of the carbon source as was the case with the reference example, and it was continuously charged at a flow rate of 7.4 NL/minute. A molybdenum and cobalt base catalyst carried on magnesium oxide having an average particle diameter of 0.1  $\mu\text{m}$  or less was activated in an inert gas and then charged at a rate of 15 g/min. The reaction temperature was set to 800°C, and the reaction pressure was set to an atmospheric pressure to continuously carry out the reaction at a rotating speed of 1 rpm. The total amount of the reacted gas was cooled in a cooler 7 to recover unreacted components and oxygen-containing hydrocarbons and then recycled to the reaction system after moisture was removed by a moisture separator

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25   11. The reacted gas corresponding to 50 % of argon gas

contained in the reacted gas at the outlet of a cooler 7  
was recycled, and the ~~remained~~remaining gas was sent to  
a waste gas-treating system. The carrier gas in the  
furnace comprised 3 NL/min as a newly charged portion and  
5 3 NL/min as a recycled portion.

As a result of the reaction, the catalyst and crude  
CNT which were collected in a CNT-collecting tank were  
19.6 g/min, and a-CNT content in the crude CNT was 4.7  
g/min. The CNT yield was more improved by 0.7 g/min than  
10 the case where recycling was not carried out, and an  
amount of argon charged was reduced by 50 %.

#### Industrial Applicability

The present invention is a process in which a fine  
15 carbon fiber can continuously and stably be produced at a  
high yield and a low cost, and it is suited for producing  
a carbon nanotube having high quality.



## ABSTRACT OF THE DISCLOSURE

Provided is a process for producing a fine carbon fiber by a method of thermal decomposition of at least one organic compound containing ~~VIBan~~ IUPAC group 16 element in the periodic table ~~in a molecule~~ using a ultra fine particles ~~comprising of~~ at least one transition metal as a catalyst, wherein a gas obtained by separating a fine carbon fiber from a gas coming out from a reaction furnace is cooled to further collect the fine carbon fiber still present in the gas. ~~then~~ After cooling, at least a part or the total amount of the above gas is cooled again to remove unwanted condensates and by-products after which the condensed components contained in the reacted gas, and then the above gas is recycled to the reaction furnace. ~~water~~ Water and the like are then separated from the condensate to further recycle the unreacted raw material organic compound removed during condensation.